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Procedures for the determination of stable elements in construction materials from the nuclear reactors at Risø National Laboratory

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Abstract (max. 2000 char.): Methods for the accurate determination of stable isotopes of elements in construction materials with relevance to the work of the Danish Decommissioning have been developed.

Prior to the analysis the elements of interest must be released from the construction materials and this is done with several different digestion methods. For the analysis of aluminium, lead, graphite and steels the samples are digested with mineral acids and microwave heating at increased pressures in a sealed teflon vessel. The aluminium, lead and steel are fully dissolved after the digestion procedure whereas graphite is chemically inert to the acid treatment used, but the elements of interest are extracted from the graphite quite efficiently. Concrete is digested with open-vessel heating in a Modblock™ digesting unit in a two step procedure involving 40% HF followed by 32% HNO_3. The heavy barite concrete is first treated as the concrete samples but a large residue of poorly soluble sulphates (mainly $BaSO_4$) is left. The residue is fused with $NaOH/Na_2CO_3$ at 575°C and after some work up the product from the fusion is dissolved in dilute HNO_3.

After the release of the elements from the materials, the samples are analysed by ICP-OES and ICP-MS multi-element analysis. In general the following elements are of interest to DD; Ag, Ba, Ca, Co, Eu, Fe, Li, Mo, Nb, Ni, Sm, Th and U. For graphite, steel, concrete and heavy concrete, analytical methods for the determination of all 13 elements have been developed (except Ca in steel). For aluminium and lead methods for the determination of Ag, Co, Li, Nb, Ni and U, as well as Ba in the lead have been developed.

When possible the methods have been verified against certified reference materials and calibration with standards additions and internal standard corrections have been used to correct for matrix effects most efficiently. The accuracy has also been checked with spikes when reference materials are not available. For the aluminium, lead, graphite and stainless steel, reference materials are available and used in the development. A Portland cement reference material is used in the development of the analytical methods for concrete material, whereas no reference material is available for the method development for the heavy concrete material. Whenever reference materials are used good agreement between measured and certified concentrations is observed.

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Preface

In the decommissioning of nuclear facilities, the inventory of radioactive elements in the various materials needs to be assessed for the classification of the nuclear waste, as well as the deposit of the nuclear waste. A part from components from the reactor cores and contaminations from leaking fuel (which is not relevant for the Danish reactors), the main radioactivity in the reactors is due to neutron activation of the graphite and other construction materials, such as aluminium, lead, steel and stainless steel, ordinary concrete and various types of heavy concrete.

An important tool in the assessment of the radioactivity in the construction materials is a modelling analysis of the activity. To do this kind of modelling, it is important to know the integrated neutron flux that the material has experienced during the operation of the reactor, the concentrations of the stable parent isotopes as well as all significant nuclear reactions for the production of the radioactive isotopes.

Only radioisotopes with significant half life are important in a disposal context, and only a small number of elements present at major or trace level need to be analysed. Besides N and Cl (not included here) the most significant elements are: Li, Ca, Fe, Co, Ni, Nb, Mo, Ba, Sm, Eu, Th and U.

The report describes work done for the Danish Decommissioning (DD). The aim of this work is the development of accurate methods for the determination of stable isotopes of elements relevant to DD using ICP-MS and ICP-OES.

1 Analytical methods

In the Radioecology programme at Risø National Laboratory we have the possibility of doing multi-element analyses by inductively coupled plasma (ICP) techniques coupled with detectors based on mass spectrometry (MS) and optical emission spectrometry (OES). These methods have been used for the analysis of stable isotopes of several elements in construction materials for DD.

1.1 Instrumentation

Plasmatrace 2 (ICP-MS). The Plasmatrace 2 is a high resolution sector mass spectrometer with BE geometry (magnetic sector before electric sector). The resolution is limited to 10.000 and can be controlled automatically by the software. ICP-MS with a mass spectrometer capable of high resolution makes it possible to separate isobaric molecular interferences from the analysed element in many instances.

Varian Vista Pro (ICP-OES). The Varian Vista Pro is capable of detecting emitted light with a charge coupled device detector yielding 98% wavelength coverage in the wavelength range 167-785 nm. The instrument uses axial view of the plasma, which increases the sensitivity of the analytical technique by a factor of 2 to 30 compared to radial view of the plasma.[1] Approximately 70 elements can be detected.

1.2 ICP spectrometry[2]

Attributes: ICP spectrometry is a technique that offers rapid, multi-element detection with low detection limits (MS – ppt or lower, OES – ppb or lower). The dynamic range is wide (5-6 orders of magnitude) and the precision is good. The technique is applicable for gases, liquids and solids.

Problems: There can be spectral interferences as well as matrix effects from solvents, acids and concomitant elements. The problem of spectral interferences can be reduced with high resolution spectrometers. High concentrations of concomitant elements (the matrix) and in particular easily ionisable elements (e.g. Ca, Na, Al) can lead to signal depression or enhancement compared to the calibration standards[3] and the signal intensities also change with the acid identity and concentration.[4] The sample introduction from the spray chamber to the plasma is inefficient unless specially designed equipment is used (<2% with a standard nebuliser).

1.2.1 Sample Inlet System

An overview of a generic ICP-system is shown on the left hand side in figure 1. The sample inlet system consists of a peristaltic pump connected to a nebuliser. The nebuliser produces an aerosol that is sprayed into the spray chamber, and in the spray chamber the smallest aerosols follow the gas flow into the plasma. At Risø we have the choice between pneumatic and ultrasonic nebulisation. Ultrasonic nebulisation produces a better aerosol (smaller droplets), which gives a more efficient sample transport to the plasma

1 Brenner, I. B. and Zander, A. T., Spectrochim. Acta B, 55 (2000), p. 1195

2 Olesik, J. W., Anal. Chem., 63 (1991), p. 12A

3 Brenner, I. B., Zander, A., Cole, M. and Wiseman, A., J. Anal. At. Spectrom., 12 (1997), p. 897

4 Todolí, J. L. and Mermet, J. M., Spectrochim. Acta B, 55 (1999), p. 895

and thereby better sensitivity, but matrix effects from concomitant elements and acids can increase.[5]

In the spray chamber three processes dominate, namely collisions with the walls, droplet-droplet collisions and evaporation from the droplets and the walls. Droplet collisions are the primary process for a low sample uptake from the spray chamber to the plasma. Evaporation from the walls may cause matrix effects if the walls are not conditioned with the sample prior to the analysis.[6]

1.2.2 The Argon Plasma

In the right hand side of figure 1 is shown a schematic overview of an Argon plasma. The aerosols are desolvated and atomised in the hot plasma, which is sustained by kW radio frequency power. Elements with ionisation potentials less than 8-9 eV mainly exist as ions in the plasma. ICP-OES relies on emission of light from *excited* atoms and/or ions, whereas ions are detected in ICP-MS without any reference to the excitation state of the ions. Changes in the atom/ion populations in the plasma can therefore have different impact on the analysis depending on the method of detection.

In ICP-OES the continuum background emission is a result of ion/electron recombination by emission of light. In ICP-MS the background counts are very low yielding high sensitivity.

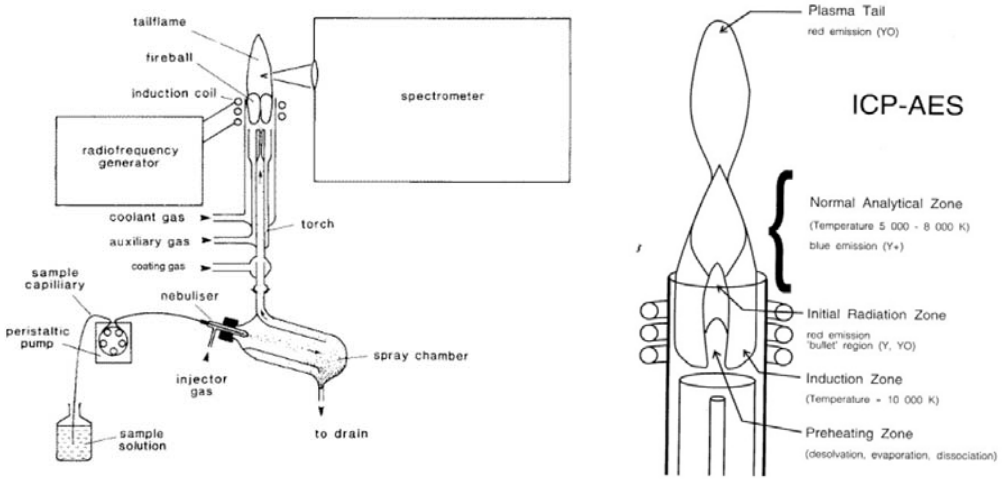

Figure 1 Overview of a radial ICP-OES system (left) and the ICP plasma (right).

1.2.3 OES vs. MS Detection

Optical emission spectrometry with the Varian Vista Pro system offers fast multi-element analysis. It is possible to analyse 73 elements in 35 seconds including a 25 sample uptake time. There are many analytical lines for each element, which may increase the confidence in the analytical result and it is almost always possible to identify an interference free emission line for a given element. This may be a very time consuming selection process, though. The ICP-OES instrument is very robust and if possible, is used in preference to the ICP-MS instrument.

5 Carré, M., Lebas, K., Marichy, M., Poussel, E. and Mermet, J. M., Spectrochim. Acta B, 50 (1995), p. 271

6 Stewart, I. I. and Olesik, J. W., *J. Anal. At. Spectrom.*, **13** (1998), p. 843

Mass spectrometry with the Plasmatrace 2 system offers very low detection limits much better than the ICP-OES instrument. The combination of high resolution mass detection with relatively few analytical lines for each element reduces spectral interferences from molecular ions. A mass resolution of 3000 (or better) facilitates separation of molecular interferences such as $^{40}Ar^{12}C^{+}$ (m/z 51,962) from $^{52}Cr^{+}$ (m/z 51,941), $^{35}Cl^{16}O^{+}$ (m/z 50,964) from $^{51}V^{+}$ (m/z 50,944), $^{40}Ar^{15}N^{+}$ (m/z 54,962) from $^{55}Mn^{+}$ (m/z 54,938) and $^{40}Ar^{16}O^{+}$ (m/z 55,957) from $^{56}Fe^{+}$ (m/z 55,935). C- and Cl-containing interferences most likely arise from the sample matrix and it is possible to eliminate these interferences by a careful sample digestion (e.g. avoid HCl and oxidize carbon to CO_2). $^{40}Ar^{16}O^{+}$ and $^{40}Ar^{15}N^{+}$ are more or less natural components in the plasma and are difficult to avoid. The main disadvantage with high resolution mass detection is the accompanying reduction of the ion beam intensity and thereby loss of sensitivity.

2 Determination of Ag, Co, Li, Nb, Ni and U in aluminium samples

2.1 Procedure

2.1.1 Digestion

0.25 g of Al is dissolved in 10 ml 1:1 mixture of 65% HNO_3/H_2O with microwave heating in a microwave oven. The type of microwave oven used for all the methods developed is a MDS-2000 from CEM Corporation Matthews (North Carolina, USA). The digestion is pressure controlled in 2 steps (~10 mins @120 psi and 15 mins @150 psi, 90% power for 12 liners). If the Al is not fully dissolved after this procedure, a second digestion with the same parameters should be done. The sample is transferred with 2*10 ml H_2O and weighted into in a polyethylene container. Total weight of the digested sample should be ~30 g. It is preferable to digest three sub-samples to evaluate sample heterogeneity and 3 blind samples and certified reference materials (CRMs) (BAM 310 (Al 99.85 Mg 1) and/or BAM 311 (Al Cu Mg2)) for the quality control.

2.1.2 Analysis

ICP-OES analysis is used for the determination of ppm levels of Li, Co and Ni in the samples. The samples are diluted by a factor of two and calibration by standard additions is used with 10, 20 and 200 ppb spikes of a multi-element standard containing the elements of interest. The samples contains ~5 vol% HNO_3 after dilution. For the OES analysis 1.2 kW power and 0.9 L/min nebuliser gas flow is used. For the analysis of trace elements 60 s integration time and two replicates are measured to get a good sensitivity with 5 ml sample volume.

The elements are analyzed at the following wavelengths (nm) as the sensitivities of the selected lines are sufficient and the amounts of interferences are not causing any problems.

Co 228.615, 231.160

Ni 216.555, 231.604

Li 670.783

ICP-MS analysis is used for the determination of sub-ppm levels of Li and Co and for the determination of Nb, Ag and U in the Al. The samples are diluted 20 times prior to analysis and calibrated by standard additions of 0.1, 0.5, 1 and 2 ppb. Sc, Rh and Th are

used as internal standards in 1-2 ppb concentration. If Th is to be determined in the Al, Bi-209 can serve as a good alternative internal standard for Th and U. The samples contain ~0.5% HNO_3 after dilution. Standard set-up of the ICP-MS instrument is used and the instrument stability is checked prior to analysis.

All the elements except Li and Ag are mono-elemental for analytical purposes, which mean that only one m/z ratio is sufficiently abundant. For Lithium both isotopes (m/z 6 and 7) are used in the analysis and for Ag m/z 107 has large interferences for the BAM 310/311 CRMs due to the formation of ZrO^+. The elements are analyzed at the following m/z ratios:

Li m/z 6 and 7	Rh m/z 103
Sc m/z 45 (4000 resolution)	Ag m/z 109
Co m/z 59 (4000 resolution)	Th m/z 232
Nb m/z 93	U m/z 238.

2.2 Results

Aluminium samples supplied from Danish Decommissioning (DD) were analyzed together with the BAM 310 and BAM 311 certified Aluminium reference materials. The results are given in Table 1.

Table 1 Results of the analysis of aluminium.

Aluminium

ELEMENT	SAMPLE	N	MS	OES	CERT	LOD
Cobalt	Al(3)	6	**1.44±0.09**	**1.8±0.2**		
	BAM 310	3	**9.8±0.3**	**11.1±0.3**	9.0±2.3	**Co-59 0.2**
	BAM 311	3	**-**	**10.5±0.6**	11.5±1.0	
Lithium	Al(3)	6	**<LOD**	**<LOD**		
	BAM 310	3	**3.4±0.2**		3.66±0.12	**Li-6 0.06**
	BAM 311		**-**			
Nickel	Al(3)	6	**-**	**39.2±1.4**		
	BAM 310	3	**-**	**24.1±0.4**	24.4±1.4	
	BAM 311	3	**-**	**496±17**	519±9	
Niobium	Al(3)	6	**0.108±0.002**	-		
	BAM 310	3	**0.027±0.001**	**-**		**Nb-93 0.02**
	BAM 311	3	**-**	**-**		
Silver	Al(3)	6	**<LOD**	-		
	BAM 310	3	**<LOD**	**-**		**Ag-109 0.07**
	BAM 311	3	**-**	**-**		
Uranium	Al(3)	6	**1.27±0.06**	-		
	BAM 310	3	**1.34±0.04**	**-**	*(2.2)*	**U-238 0.12**
	BAM 311	3	**-**	**-**		

All concentrations are in ppm. Uncertainty = 1σ
BAM 310/311 = Certified reference materials. Uncertainty = 2σ
N = Number of samples digested
MS = ICP-MS analysis
OES = ICP-OES analysis
LOD = Limit of detection
CERT = Certified value. Number in ( ) is for informational value only

2.3 Conclusion

The analysis of traces of Ag, Li, Co, Ni, Nb and U in Aluminium samples can be done when combining microwave digestion with ICP-OES and ICP-MS analysis.

The agreement between the measured and the certified values in the two CRMs is very good. The measured concentration of U in BAM 310 is 40% lower than the informational value given from BAM. The reason for this discrepancy is not fully

understood. The digestion procedure yields a clear solution and the analysis is done by standard additions analysis combined with internal standardization with Th-232 to correct for drift and matrix effects. Therefore 40% deviation would not be expected especially when looking at the good agreement between the remainder of the certified elements.

3 Determination of Ag, Ba, Co, Li, Nb, Ni and U in lead samples

3.1 Procedure

3.1.1 Digestion

0.25 g of Pb is dissolved in 10 ml 1:1 mixture of 65% HNO_3/H_2O with microwave heating. The digestion is pressure controlled in 2 steps (~30 mins @120 psi and 15 mins @150 psi, 90% power for 12 liners). If the Pb is not fully digested after that procedure a second digestion with the same parameters should be done. The sample is transferred with 2*10 ml H_2O and weighted into in a polyethylene container. Total weight of the digested sample should be ~30 g. It is preferable to digest three sub-samples to evaluate sample heterogeneity and three blind samples and a reference material (BCR 288b; lead with added impurities) for the quality control.

3.1.2 Analysis

ICP-OES analysis is used for the determination of ppm levels of Ag and Ni in the samples. The samples are diluted by a factor of 5 and calibration by standard additions is used with 10, 50 and 200 ppb spikes of a multi-element standard containing the elements of interest. The samples contains ~2 vol% HNO_3 after dilution. Alternatively, external calibration combined with internal standardization by Y or Sc can be used with good accuracy. For the OES analysis 1.2 kW power and 0.9 L/min nebuliser gas flow is used. Integration time is 60 s and two replicates are measured to get a good sensitivity with 5 ml sample volume.

The elements are analyzed at the following wavelengths (nm) as the sensitivities of the selected lines are sufficient and the amounts of interferences are not causing any problems.

Ag 328.068, 338.289

Ni 216.555, 231.604

ICP-MS analysis is used for the determination of trace amounts of Ba, Co, Li, Nb and U in the Pb. The samples are diluted 20 times prior to analysis and calibrated by standard additions of 0.1, 0.5, 1 and 5 ppb. Be, Sc, In and Th are used as internal standards in 1-2 ppb concentration. The samples contain ~0.5 vol% HNO_3 after dilution. Standard set-up of the ICP-MS instrument is used and the instrument stability is checked prior to analysis.

All the elements except Ba and Li are mono-elemental for analytical purposes, which mean that only one m/z ratio is sufficiently abundant. For Lithium both isotopes (m/z 6 and 7) are used in the analysis and for Ba the two most abundant ions, m/z 137 and 138 are used. The elements are analyzed at the following m/z ratios:

Li m/z 6 and 7 Be m/z 9

Sc m/z 45 (4000 resolution)

Co m/z 59 (4000 resolution)

Nb m/z 93

In m/z 115

Ba m/z 137 and 138

Th m/z 232

U m/z 238

3.2 Results

Two different lead samples supplied from DD were analyzed together with the BCR 288b certified Lead reference materials (Lead with added impurities). The results are shown in Table 2.

3.3 Conclusion

The analysis of traces of Ag, Ba, Co, Li, Nb, Ni and U in lead samples can be done when combining microwave digestion with ICP-OES and ICP-MS analysis.

The agreement between the measured and the certified values for Ag and Ni in the CRM is very good, thus suggesting that the results obtained for the analysis of Ag and Ni in the lead samples supplied from DD are accurate.

The concentration levels of Ba, Co, Li, Nb and U are very low in the Pb from DD as well as in the CRM.

Table 2 Results from the analysis of lead.

			Lead			
ELEMENT	**SAMPLE**	**N**	**MS**	**OES**	**CERT**	**LOD**
Barium	Pb(1)	2	**0.89±0.15**			
	Pb(2)	1	**0.25**			**Ba-138 0.12**
	BCR 288b	3	**0.15±0.03**			
Cobalt	Pb(1)	2	**<LOD**			
	Pb(2)	1	**<LOD**			**Co-59 0.05**
	BCR 288b	3	**<LOD**			
Lithium	Pb(1)	2	**<LOD**			
	Pb(2)	1	**<LOD**			**Li-7 0.07**
	BCR 288b	3	**<LOD**			
Nickel	Pb(1)	2	**-**	**3.3±0.3**		
	Pb(2)	1	**-**	**2.2±0.3**		
	BCR 288b	3	**-**	**5.2±0.6**	4.6±0.1	
Niobium	Pb(1)	2	**<LOD**	-		
	Pb(2)	1	**0.001**	**-**		**Nb-93 0.7 ppb**
	BCR 288b	3	**<LOD**	**-**		
Silver	Pb(1)	2	-	**20.6±1.6**		
	Pb(2)	1	**-**	**5.9±0.6**		**Ag-107 0.2**
	BCR 288b	3	**-**	**30.3±1.0**	30.5±0.5	
Uranium	Pb(1)	2	**<LOD**	-		
	Pb(2)	1	**<LOD**	**-**		**U-238 0.025**
	BCR 288b	3	**<LOD**	**-**		

All concentrations are in ppm unless noted otherwise
Uncertainty = 1σ
BCR 288b = Certified reference material. Uncertainty = 2σ
N = Number of samples digested
MS = ICP-MS analysis
OES = ICP-OES analysis
LOD = Limit of detection
CERT = Certified value. Number in ( ) is for informational value only

4 Determination of Ag, Ba, Ca, Co, Eu, Fe, Li, Mo, Nb, Ni, Sm, Th and U in graphite samples

4.1 Procedure

4.1.1 Extraction

This analytical procedure was developed with the use of three synthetic graphite reference materials (RMs) (KD1, LD4 and KD6; Synthetic graphite powders with added impurities from Breitländer GmbH). To fully dissolve graphite hot perchloric/sulfuric acid or ashing followed by acid dissolution is required. Ashing was not considered to be an efficient procedure in our labs. And special equipment for the handling of hot perchloric/sulfuric acid solutions is not available for large sample loads. Therefore an acid extraction procedure was tested on three commercial graphite reference materials and found to be successful.

0.10 g of graphite is extracted in a sealed vessel with increased pressure and microwave heating in two stages. First stage involves addition of 5 ml 65% HNO_3 and heating in 3 steps (5 mins. @100 psi, 5 mins. @150 psi and 5 mins. @200 psi, 100% power with 12 liners). The samples are allowed to cool down to room temperature and 5 ml 40% H_2O_2 is added and the solutions stand for 15 mins. before 0.1 ml 40% HF is added. The second extraction stage involves the same 3 steps as mentioned above. The graphite samples are not fully digested, but this extraction procedure has shown to be sufficient. The sample is transferred with 2*10 ml H_2O and weighted into in a polyethylene container. Total weight of the digested sample should be ~30 g. It is preferable to digest three sub-samples to evaluate sample heterogeneity and three blind samples and samples of the reference materials for the quality control.

4.1.2 Analysis

ICP-OES analysis is used for the determination of ppm levels of Ba, Co, Li, Mo and Ni in the samples. The samples are diluted by a factor of 2 to 5 ml total volume and external calibration from 0.001–1 ppm is used with a multi-element standard containing the elements of interest. The samples contain ~5.5 vol% HNO_3 after dilution. For the OES analysis 1.2 kW power and 0.9 L/min nebuliser gas flow is used. Integration time is 60 s and two replicates are measured to get a good sensitivity with 5 ml sample volume.

The elements are analyzed at the following wavelengths (nm) as the sensitivities of the selected lines are sufficient and the amounts of interferences are not causing any problems.

Ba 233.527, 455.403, 493.408

Co 230.786, 237.863

Li 670.783

Mo 202.032, 204.598, 284.824

Ni 216.555, 227.021, 230.299

ICP-MS analysis is used for the determination of trace amounts of Ag, Ba, Co, Eu, Li, Mo, Nb, Ni, Sm, Th and U in the graphite. The samples are diluted 4 times prior to analysis and calibrated by external standard 0.1-2 ppb. In and Bi are used as internal

standards in 1-2 ppb concentration. The samples contain ~2.7% HNO_3 after dilution. Standard set-up of the ICP-MS instrument is used and the instrument stability is checked prior to analysis.

The elements are analyzed at the following m/z ratios:

Li m/z 6

Co m/z 59 (4000 resolution)

Ni m/z 60

Nb m/z 93

Mo m/z 95, 98, 100

Ag m/z 107, 109

In m/z 115

Ba m/z 134, 135

Pr m/z 141

Nd m/z 143, 145

Sm m/z 147, 149

Eu m/z 151, 153

Gd m/z 157, 158

Tb m/z 159

Dy m/z 161, 163

Ho m/z 165

Er m/z 166, 167

Tm m/z 169

Yb m/z 171, 172, 173

Lu m/z 175

Bi m/z 209

Th m/z 232

U m/z 238

The added lanthanide elements (Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) are used to evaluate the accuracy of the measured concentrations of Eu and Sm.

4.2 Results

Results for the elements of interest to DD are shown in Table 3 and the measured values for the lanthanide elements are given in Table 4. Three different graphite reference materials were used for the development of this method. Concentrations of Al, Ca, *Co*, Cr, Cu, Fe, Mg, Mn, *Mo*, Ni, *Pb*, *Sr*, *Ti*, *V*, *Zn* and *Zr* are given in the certificates, but only informational values based on neutron activation analysis data are given for the elements listed above in italics. The developed method was therefore also checked against elements that are not of any particular interest to DD as a part of the quality control (i.e. Al, Ca, Cr, Cu, Fe, Mg, Mn, Pb, Sr, Ti, V, Zn and Zr). These values are reported in Table 5.

Table 3 Results from the analysis of graphite.

Graphite

ELEMENT	SAMPLE	N	MS	OES	REF	LOD
Barium	KD1	7	**6.1±0.5**	**6.4±0.7**		
	LD4	6	**7.9±0.2**	**8.0±0.2**		**Ba-135 0.03**
	KD6	7	**5.8±0.2**	**5.7±0.2**		
	DD Graphite	3	**5.1±1.0**	**5.4±1.0**		
Cobalt	KD1	7	**0.24±0.02**		*(0.19)*	
	LD4	6	**0.13±0.01**		*(0.11)*	**Co-59 0.012**
	KD6	7	**0.033±0.006**		*(0.03)*	
	DD Graphite	3	**0.016±0.001**			
Europium	KD1	7	**0.016±0.001**			
	LD4	6	**0.033±0.001**			**Eu-151 0.02**
	KD6	7	**0.020±0.001**			
	DD Graphite	3	**0.024±0.003**			
Lithium	KD1	7	**4.2±0.3**	**3.7±0.4**		
	LD4	6	**3.5±0.3**	**3.4±0.1**		**Li-7 0.07**
	KD6	7	**3.7±0.2**	**3.1±0.1**		
	DD Graphite	3	**0.73±0.12**	**0.53±0.04**		
Molybdenum	KD1	7	**1.0±0.1**	**1.2±0.2**	*(0.95)*	
	LD4	6	**0.61±0.04**	**0.7±0.2**	*(0.62)*	**Mo-98 0.01**
	KD6	7	**0.35±0.02**	**0.5±0.1**	*(0.39)*	
	DD Graphite	3	**0.52±0.02**	**0.6±0.2**		
Nickel	KD1	7	**6.7±0.6**	**6.5±0.8**	*6.0±0.9*	
	LD4	6	**6.1±0.3**	**6.2±0.5**	*5.5±0.4*	**Ni-60 0.1**
	KD6	7	**2.1±0.1**	**1.8±0.3**	*2.0±0.1*	
	DD Graphite	3	**3.4±0.3**	**3.6±0.2**		
Niobium	KD1	7	**0.13±0.01**			
	LD4	6	**0.13±0.01**			**Nb-93 0.04**
	KD6	7	**0.074±0.004**			
	DD Graphite	3	**0.17±0.10**			
Samarium	KD1	7	**0.087±0.005**			
	LD4	6	**0.091±0.003**			**Sm-147 0.03**
	KD6	7	**0.074±0.003**			
	DD Graphite	3	**0.22±0.02**			
Silver	KD1	7	**<LOD**			
	LD4	6	**<LOD**			**Ag-107 0.05**
	KD6	7	**<LOD**			
	DD Graphite	3	**0.11±0.02**			
Thorium	KD1	7	**0.082±0.005**			
	LD4	6	**0.071±0.004**			**Th-232 0.02**
	KD6	7	**0.040±0.003**			
	DD Graphite	3	**0.032±0.007**			
Uranium	KD1	7	**0.030±0.001**			
	LD4	6	**0.033±0.002**			**U-238 0.02**
	KD6	7	**0.019±0.001**			
	DD Graphite	3	**0.025±0.004**			

All concentrations are in ppm unless noted otherwise
Uncertainty = 1 standard deviation
KD1, LD4, KD6 = Reference materials
N = Number of samples digested
MS = ICP-MS analysis
OES = ICP-OES analysis
LOD = Limit of detection
REF = Reference value. Number in ( ) is for informational value only

Table 4 Determination of lanthanides in the graphite.

	Graphite		
ELEMENT	**SAMPLE**	**N**	**MS**
Dy	KD1	7	**0.041±0.002**
	LD4	6	**0.016±0.002**
	KD6	7	**0.018±0.001**
	DD Graphite	3	**0.025±0.007**
Gd	KD1	7	**0.047±0.004**
	LD4	6	**0.024±0.001**
	KD6	7	**0.023±0.001**
	DD Graphite	3	**0.023±0.006**
Ho	KD1	7	**0.0074±0.0006**
	LD4	6	**0.0031±0.0003**
	KD6	7	**0.0032±0.0002**
	DD Graphite	3	**0.0045±0.0013**
Lu	KD1	7	**0.0026±0.0002**
	LD4	6	**0.0015±0.0001**
	KD6	7	**0.0015±0.0002**
	DD Graphite	3	**0.0015±0.0003**
Pr	KD1	7	**0.055±0.003**
	LD4	6	**0.025±0.002**
	KD6	7	**0.026±0.002**
	DD Graphite	3	**0.025±0.007**
Tb	KD1	7	**0.0069±0.0005**
	LD4	6	**0.0034±0.0001**
	KD6	7	**0.0032±0.0002**
	DD Graphite	3	**0.0036±0.0010**
Tm	KD1	7	**0.0043±0.0002**
	LD4	6	**0.0028±0.0003**
	KD6	7	**0.0022±0.0002**
	DD Graphite	3	**0.0036±0.0005**
Yb	KD1	7	**0.013±0.001**
	LD4	6	**0.040±0.002**
	KD6	7	**0.022±0.001**
	DD Graphite	3	**0.021±0.002**

All concentrations are in ppm unless noted otherwise
Uncertainty = 1 standard deviation
KD1, LD4, KD6 = Reference materials
N = Number of samples digested
MS = ICP-MS analysis

Table 5 Determination of other stable elements in the graphite.

	Graphite			
ELEMENT	**SAMPLE**	**N**	**OES**	***REF***
Al	KD1	7	**19±3**	*12±2*
	LD4	6	**46±4**	*33±7*
	KD6	7	**9±3**	*8.4±3.4*
	DD Graphite	3	**56±6**	
Ca	KD1	7	**92±13**	*74±25*
	LD4	6	**148±5**	*126±22*
	KD6	7	**91±4**	*79±15*
	DD Graphite	3	**261±79**	
Cr	KD1	7	**3.4±0.7**	*3.2±0.4*
	LD4	6	**3.6±0.1**	*3.4±0.6*
	KD6	7	**0.33±0.01**	*0.44±0.22*
	DD Graphite	3	**34±39**	
Cu	KD1	7	**1.2±0.4**	*1.0±0.1*
	LD4	6	**1.2±0.1**	*1.3±0.2*
	KD6	7	**0.43±0.04**	*0.6±0.2*
	DD Graphite	3	**0.43±0.12**	
Fe	KD1	7	**471±49**	*428±60*
	LD4	6	**146±3**	*149±12*
	KD6	7	**40.2±1.3**	*37±4*
	DD Graphite	3	**64±10**	
Mg	KD1	7	**8±2**	*(6.7)*
	LD4	6	**12.3±0.2**	*(7.5)*
	KD6	7	**1.9±0.1**	
	DD Graphite	3	**6±4**	
Mn	KD1	7	**61±6**	*56±11*
	LD4	6	**3.5±0.1**	*3.5±0.8*
	KD6	7	**4.7±0.2**	*4.3±0.6*
	DD Graphite	3	**0.87±0.14**	
Pb	KD1	7	**1.0±0.2**	*(1.3)*
	LD4	6	**<LOD**	*(1.1)*
	KD6	7	**<LOD**	*(1.2)*
	DD Graphite	3	**<LOD**	
Sr	KD1	7	**1.9±0.3**	*(1.8)*
	LD4	6	**2.6±.01**	*(2.7)*
	KD6	7	**1.6±0.1**	*(1.9)*
	DD Graphite	3	**2.3±0.4**	
Ti	KD1	7	**9.6±1.0**	*(53)*
	LD4	6	**-**	*(49)*
	KD6	7	**-**	*(51)*
	DD Graphite	3	**-**	
V	KD1	7	**6.4±0.7**	*(6.6)*
	LD4	6	**3.4±0.2**	*(4.3)*
	KD6	7	**3.3±0.1**	*(4.9)*
	DD Graphite	3	**167±21**	
Zn	KD1	7	**4.4±3.2**	*(2.3)*
	LD4	6	**3.0±1.1**	*(8.6)*
	KD6	7	**0.8±0.6**	*(1.7)*
	DD Graphite	3	**10±12**	
Zr	KD1	7	**4.3±0.6**	*(7.5)*
	LD4	6	**-**	*(8.6)*
	KD6	7	**-**	*(6.0)*
	DD Graphite	3	**-**	

All concentrations are in ppm unless noted otherwise
Uncertainty = 1 standard deviation
KD1, LD4, KD6 = Reference materials
N = Number of samples digested
MS = ICP-MS analysis
OES = ICP-OES analysis
LOD = Limit of detection
REF = Reference value
Number in ( ) is for informational value only

4.3 Conclusion

In Table 3 the results of elements in interest for DD has been given. Only three elements (Co, Mo and Ni) in the RMs have reference values, which makes control of the accuracy difficult for many of the elements. The agreement between reference concentrations and the measured concentrations for Co, Mo and Ni is very good for all three RMs, and in general determinations of concentrations with two independent analytical techniques (ICP-MS and ICP-OES) agree well.

To make a more extensive control of the quality of the developed analytical method several lanthanide elements where analysed as a second check on the Eu and Sm concentrations, since ratios of the concentrations of the lanthanide elements for natural materials are well known. Secondly the concentrations were determined for the additional stable elements, where the reference concentration values are given in the three RMs. The agreement between measured values and reference values are good for Al, Ca, Cr, Cu, Fe, Mg (except LD4), Mn, Pb, Sr and V. It is not possible to measure Ti with a satisfactory result and Zr gives a too low concentration in the KD1 graphite material, which most likely is due to problems with the dissolution and extraction. Therefore those elements were not measured for the remainder of the graphite materials in this study. Ti and Zr are known to be very difficult to dissolve (refractory elements) and this drawback of the developed method should be kept in mind if some of the elements of interest to DD have similar dissolution properties. The measured concentrations for Zn are not all in agreement with the reference values and the relative standard deviations are large in general, which is due to a significant contamination of Zn from the analytical procedure. This is a Zn specific problem and should not be a problem for any of the elements of interest to DD.

All the graphite reference materials were also analysed after an extraction procedure involving concentrated HNO_3/HCl (4:1) with similar results for all the elements that could be analysed by ICP-OES, but the stability of the solutions were not good enough.

In conclusion this method gives satisfactory results for the large majority of elements where reference values for the RMs exist, but it is not possible to verify the accuracy of the analysis of Ag, Ba, Eu, Li, Nb, Sm, Th and U. The concentrations of the elements are in the low ppm to low ppb level in general.

5 Determination of Ag, Ba, Co, Eu, Fe, Li, Mo, Nb, Ni, Sm, Th and U in steel and iron samples

5.1 Procedure

5.1.1 Digestion

This analytical procedure was developed with the use of two standard reference stainless steels from NIST (SRM 160b Cr 18–Ni 12–Mo 2 (AISI 316) and SRM 123c Cr 17–Ni 11–Nb 0.6 (AISI 348)). 0.2 g steel is dissolved in a mixture of 3 ml 30% HCl, 1 ml 65% HNO_3 and 0.1 ml 40% HF with microwave heating. The digestion is pressure controlled in three steps (~10 mins @100 psi 10 mins @150 psi and 30 mins @200 psi. 100% power for 12 liners). The sample is transferred with 2*10 ml H_2O and weighted into in a polyethylene container. Total weight of the digested sample should be ~30 g. It is

preferable to digest three sub-samples to evaluate sample heterogeneity and three blind samples as well as certified reference materials for the quality control.

5.1.2 Analysis

ICP-OES analysis is used for the determination of ppm to % levels of Ba, Co, Fe, Mo, Nb and Ni in the samples. To determine all elements in % concentrations the samples are diluted by a factor of 200 in 1% HNO_3 to 10 ml total volume, and external calibration from 0.01–10 ppm is used with a multi-element standard containing the elements of interest. For the analysis of Ba, Co, Mo and Ni as well as other elements in ppm concentrations, the solutions are analysed 10 times diluted and undiluted with calibration from 0.001–1 ppm (in 3% HCl, 2% HNO_3). Sc 255.235 nm is used as internal standard (~100 ppb added to each sample) to correct for matrix effects. For OES analysis 1.2 kW power and 0.9 L/min nebuliser gas flow is used. Integration time is 60 s and three replicates are measured.

The elements are analyzed at the following wavelengths (nm) as the sensitivities of the selected lines are sufficient and the amounts of interferences are not causing any problems.

Ba 493.408, 614.171

Co 194.064, 201.151, 202.236, 231.160

Fe 234.350, 238.204, 239.563, 259.940

Mo 202.032, 203.846, 204.598, 277.539

Nb 229.568, 229.568, 269.706, 271.663, 295.088

Ni 216.555, 221.648, 227.021, 231.604

ICP-MS analysis is used for the determination of trace amounts of Ag, Ca, Eu, Li, Nb, Sm, Th and U in the steel samples. The samples are diluted 50 times in 1% HNO_3 prior to analysis and calibrated by standard addition of 0.05–0.5 ppb multi-element standards containing the elements of interest. Rh, In and Bi are used as internal standards in 1-2 ppb concentration. Standard set-up of the ICP-MS instrument is used and the instrument stability is checked prior to analysis.

The elements are analyzed at the following m/z ratios:

Li m/z 6, 7

Ca m/z 44 (4000 resolution)

Nb m/z 93

Rh m/z 103 (4000 resolution)

Ag m/z 107, 109

In m/z 115

Sm m/z 147, 149

Eu m/z 151, 153

Bi m/z 209

Th m/z 232

U m/z 238

5.2 Results

Results for the elements of interest to DD are shown in Table 6. Two stainless steel SRMs were used for the development of this method and for the elements where no reference values were given, the analytical procedure was checked with spikes recovery experiments. The recoveries of spikes are given in Table 6 as well. An inactive iron

sample from DR1 was analysed with the developed procedure and results are given in Table 6 as well.

Table 6 Results from the analysis of stainless steels and iron.

			Steel				
ELEMENT	**SAMPLE**	**N**	**MS**	**%REC**	**OES**	**SRM**	**LOD**
Barium	SRM 160b	10			**2.9±0.1**		
	SRM 123c	8			**2.6±0.1**		
	DR1 Iron	3					
Cobalt	SRM 160b	10			**0.107±0.003%**	*0.101±0.005%*	
	SRM 123c	8			**0.112±0.004%**	*0.12±0.01%*	
	DR1 Iron	3			**176±4**		
Europium	SRM 160b	1	**<LOD**	**101%**			
	SRM 123c	1	**<LOD**	**99%**			**Eu-151 0.005**
	DR1 Iron	3	**<LOD**				
Iron	SRM 160b	10			**64.8±0.8%**		
	SRM 123c	8			**66.2±1.2%**		
	DR1 Iron	3			**101.4±2.0%**		
Lithium	SRM 160b	1	**<LOD**	**109%**	**<LOD**		
	SRM 123c	1	**<LOD**	**104%**	**<LOD**		**Li-7 0.08**
	DR1 Iron	3	**0.32±0.07**		**0.26±0.11**		
Molybdenum	SRM 160b	10			**2.45±0.03%**	*2.38±0.01%*	
	SRM 123c	8			**0.217±0.004%**	*0.22±0.01%*	
	DR1 Iron	3			**24±11**		
Nickel	SRM 160b	10			**12.4±0.2%**	*12.26±0.05%*	
	SRM 123c	8			**11.7±0.1%**	*11.3±0.5%*	
	DR1 Iron	3			**525±67**		
Niobium	SRM 160b	10	**5.3***	**96%**	**3.8±0.3**		
	SRM 123c	8			**0.59±0.2%**	*0.65±.0.01%*	**Nb-93 0.04**
	DR1 Iron	3	**<LOD**				
Samarium	SRM 160b	1	**<LOD**	**98%**			
	SRM 123c	1	**<LOD**	**97%**			**Sm-147 0.02**
	DR1 Iron	3	**<LOD**				
Silver	SRM 160b	10	**2.0***	**103%**	**1.2±0.1**		
	SRM 123c	8	**1.7***	**105%**	**1.1±0.1**		**Ag-107 0.04**
	DR1 Iron	3	**<LOD**		**<LOD**		
Thorium	SRM 160b	1	**<LOD**	**96%**			
	SRM 123c	1	**<LOD**	**96%**			**Th-232 0.004**
	DR1 Iron	3	**<LOD**				
Uranium	SRM 160b	1	**<LOD**	**94%**			
	SRM 123c	1	**<LOD**	**98%**			**U-238 0.014**
	DR1 Iron	3	**<LOD**				

All concentrations are in ppm unless noted otherwise
Uncertainty = Standard error of the mean. 2σ for the DR1 Iron and 2σ for the SRMs
SRM 160b, 123c = Standard reference materials from NIST
N = Number of samples digested
MS = ICP-MS analysis
%REC = Spike recovery in the ICP-MS analysis
OES = ICP-OES analysis
LOD = Limit of detection
SRM = Standard reference material. Number in ( ) is for informational value only
***Only one sample of the 8-10 digestions were measured with ICP-MS**

5.3 Conclusion

The determination of elemental concentrations of Co, Mo and Ni in the two SRMs is in very good agreement with the reference concentrations. The determination of Nb in SRM 123c only recovers 91% of the certified amount and the difference between the reference and measured concentration is significant (on a 95% confidence level). A previous analysis acquired 6 days earlier of the same solutions yielded a Nb concentration of 0.64±0.02% and it therefore seems that Nb is lost on standing. Secondly the concentration of Cr, Cu and Mn was determined with a similar good agreement and the concentrations of the major constituents (Co, Cr, Cu, Fe, Mn, Mo, Nb and Ni) can account for 99.8% and 97.9% of the material for SRM 160b and 123c, respectively. The

iron acquired from DD has a different composition compared to the stainless steel SRMs from NIST (the stainless steels contain large amounts of Cr and Ni in particular), but since the digestions of the three steel/iron samples are complete and the OES analysis is sufficiently robust, it is not considered to be a problem for the accuracy of the developed method. For the ICP-MS analysis the effects of the analytical accuracy with the different sample matrices was checked with spikes of the different elements and the spike recoveries were 94-109%.

The concentrations of Ag, Eu, Nb, Sm, Th and U in the DR1 iron are below the detection limits of the developed method and the concentration level of Li was quite low. Ba was not measured with ICP-OES for the DR1 steel and could not be determined with ICP-MS and is therefore not reported.

6 Determination of Ag, Ba, Ca, Co, Eu, Fe, Li, Mo, Nb, Ni, Sm, Th and U in concrete samples

6.1 Procedure

6.1.1 Digestion

0.2 g finely crushed and homogenized concrete sample is dissolved by a two step digestion procedure in a Modblock™ digestion system (CPI International, Santa Rosa, California, USA), which is a heating block where the heating temperature can be controlled precisely up to ~130° C. The concrete sample is mixed with 10 ml 40% HF and the solution is evaporated to dryness at 120° C (~90° C in the samples) over a 4 hours period. Then the residue is dissolved in 10 ml 1:1 65% HNO_3/H_2O with heating at 90° C for 1 - 1½ hours. 20 ml H_2O is added after and heated for 10 minutes to ensure dissolution. The sample is transferred with ~2*10 ml H_2O and weighted into in a polyethylene container to 50 ml total volume. The concentration of HNO_3 in the final sample is 6-7 vol% if no serious evaporation of HNO_3 has taken place. It is preferable to digest three sub-samples to evaluate sample heterogeneity and three blind samples as well as certified reference materials for the quality control. In this method development a Portland cement certified reference material was used (Portland cement X0203, AG DER Dillinger Hüttenwerke). To our knowledge no concrete reference materials exist and Portland cement is one of the major constituents of the concrete samples from DD.

6.1.2 Analysis

ICP-OES analysis is used for the determination of ppm to % levels of Ba, Ca, Co, Eu, Fe, Li, Mo, Nb, Ni, Sm and Th in the samples. To determine all elements in % concentrations the samples are diluted by a factor of 50-100 in 1% HNO_3 to 10 ml total volume, and external calibration from 0.01–10 ppm is used with a multi-element standard containing the elements of interest. For the analysis of Co, Eu, Fe, Li, Mo, Nb, Ni, Sm and Th in ppm concentrations, the solutions are analysed with standard additions calibration with 5–200 ppb spikes. Sc 255.235 nm is used as internal standard (~1 ppm added to each sample) to correct for matrix effects. For OES analysis 1.2 kW power and 0.9 L/min nebuliser gas flow is used. Integration time is 60 s and two replicates are measured.

The elements are analyzed at the following wavelengths (nm) as the sensitivities of the selected lines are sufficient and the amounts of interferences are not causing any problems.

Ba 230.424, 233.527

Ca 183.944, 211.276, 315.887, 317.933

Co 258.033, 230.786

Eu 420.504

Fe 238.204, 238.863

Li 670.783

Mo 202.032, 203.846

Nb 210.942, 295.088

Ni 222.486, 231.604

Sm 359.259

Th 401.913

ICP-MS analysis is used for the determination of ppb to ppm levels of Ag, Eu, Mo, Nb, Sm, Th and U in the concrete samples. The samples are diluted 40-50 times in 1% HNO_3 prior to analysis and calibrated by standard addition of 0.25–5 ppb multi-element standards containing the elements of interest. In and Bi are used as internal standards in 1-2 ppb concentration. Standard set-up of the ICP-MS instrument is used and the instrument stability is checked prior to analysis.

The elements are analyzed at the following m/z ratios:

Nb m/z 93	Tb m/z 159
Mo m/z 95	Dy m/z 161, 163
In m/z 115	Ho m/z 165
Ag m/z 107, 109	Er m/z 166, 167
Ba m/z 134, 135, 136	Tm m/z 169
Pr m/z 141	Yb m/z 171, 172, 173
Nd m/z 143, 145	Lu m/z 175
Sm m/z 147, 149, 152, 154	Bi m/z 209
Eu m/z 151, 153	Th m/z 232
Gd m/z 157, 158	U m/z 238

The added lanthanide elements (Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) are used to evaluate the accuracy of the measured concentrations of Eu and Sm. Ba is determined to make a mathematical correction for BaO and BaOH interferences on Eu 151, Sm 152, Eu 153 and Sm 154. The amount of correction is evaluated with a 50 ppb Ba standard and in general the correction is less than 5% of the total signal of Eu and Sm.

6.2 Results

Results for the elements of interest to DD are shown in Table 7 and the measured values for the lanthanide elements are tabulated in Table 8. A Portland cement CRM was used for the development of this method and for the elements determined with ICP-MS the analytical procedure was checked with spikes. The recoveries of spikes are given in Table 7 as well. An inactive sample of ordinary construction concrete from DR1 was analysed with the developed procedure and results are given in Table 7 as well.

Table 7 Results from the analysis of concrete.

			Concrete			
ELEMENT	**SAMPLE**	**N**	**%REC**	**MS**	**OES**	**REF**
Barium	DD concrete	6			**448±9**	
	X0203	3			**268±6**	282.2±8.2
Calcium	DD concrete	6			**9.5%±0.2%**	
	X0203	3			**43.9%±1.0%**	46.4±0.1%
Cobalt	DD concrete	6			**7.5±0.8**	
	X0203	3			**13.6±0.6**	13.5±0.2
Europium	DD concrete	6		**0.74±0.21**	**0.92±0.03**	
	X0203	3	**111%**	**1.11±0.16**	**1.15±0.06**	
Iron	DD concrete	6			**1.40%±0.08%**	
	X0203	3			**2.39%±0.03%**	2.45±0.02%
Lithium	DD concrete	6			**18.0±0.6**	
	X0203	3			**35.3±2.4**	
Molybdenum	DD concrete	6		**1.7±0.2**	**1.3±0.2**	
	X0203	3	**108%**	**4.2±0.3**	**4.5±1.2**	4.0±0.5
Nickel	DD concrete	6			**14.7±1.7**	
	X0203	3			**26.9±3.5**	29.9±1.0
Niobium	DD concrete	6		**8.2±1.0**	**11.5±2.7**	
	X0203	3	**103%**	**6.4±1.1**	**5.0±1.0**	
Samarium	DD concrete	6		**2.5±0.4**	**3.8±0.4**	
	X0203	3	**108%**	**5.3±1.9**	**5.8±0.4**	
Thorium	DD concrete	6		**3.4±0.6**	**5.0±1.1**	
	X0203	3	**98%**	**4.9±0.8**	**3.5±0.6**	7.4±0.2
Uranium	DD concrete	6		**1.7±0.1**		
	X0203	3	**97%**	**3.1±0.7**		4.3±0.1

All concentrations are in ppm unless noted otherwise
Uncertainty = 1 standard deviation
X0203 = Certified reference material
N = Number of samples digested
%REC = Spike recovery in the ICP-MS analysis
MS = ICP-MS analysis
OES = ICP-OES analysis
REF = Reference value

Table 8 Determination of lanthanide elements in the concrete.

Concrete			
ELEMENT	**SAMPLE**	**N**	**MS**
Dy	DD concrete	6	**1.9±0.3**
	X0203	3	**3.2±0.6**
Gd	DD concrete	6	**2.9±0.9**
	X0203	3	**5.8±1.1**
Ho	DD concrete	6	**0.37±0.04**
	X0203	3	**0.64±0.11**
Lu	DD concrete	6	**0.17±0.03**
	X0203	3	**0.26±0.05**
Pr	DD concrete	6	**3.4±0.6**
	X0203	3	**5.2±0.8**
Tb	DD concrete	6	**0.34±0.05**
	X0203	3	**0.61±0.10**
Tm	DD concrete	6	**0.15±0.02**
	X0203	3	**0.22±0.03**
Yb	DD concrete	6	**1.1±0.1**
	X0203	3	**1.5±0.2**

All concentrations are in ppm unless noted otherwise
Uncertainty = 1 standard deviation
X0203 = Certified reference material
N = Number of samples digested
MS = ICP-MS analysis

6.3 Conclusion

The determined concentrations of Ba, Ca, Co, Fe, Mo and Ni in the Portland cement are in good agreement with the certified values, whereas the measured concentrations of Th and U are low. In general there is good agreement between the two analytical techniques (OES and MS) for all elements measured with both techniques independent of the matrix and the spikes of the Portland cement in the ICP-MS analysis to check the analysis of different matrix samples with only one calibration yield recoveries in the range 97-111% which is acceptable.

The Portland cement samples are not completely digested with the digestions procedure developed for the concrete samples where as the concrete samples are completely digested, which may explain the low concentrations determined for U and Th in the Portland cement CRM. A second digestion of the concrete samples and Portland cement CRM yielded Th and U concentrations of 5.0±1.0 (Th) and 2.6±0.2 (U) for the concrete samples and 2.1±1.0 (Th) and 4.0±0.1 (U) for the Portland cement CRM. Several extraction procedure developed for the concrete samples with HNO_3/HF and microwave heating yielded a U concentration of ~2.5 ppm and Th concentration of ~5.0 ppm in agreement with the measured concentrations from this reported total digestion procedure. This suggests that the determined concentrations of U and Th in the concrete are accurate whereas especially the Th determination is too low for the Portland cement CRM.

The concentrations of Eu, Li, Nb and Sm are not certified in the Portland cement and there is no quality control on those determinations except for the control of the analysis. Li is usually non-problematic to extract from these kinds of materials. Nb requires HF to dissolve and this is also one of the reasons as to why a significant volume of HF is used in the digestion. The analyses of the lanthanide elements were done to be able to check the analysis of Eu and Sm where the natural relative occurrences of these elements are known.

Ag was analysed by ICP-MS in the second digestion of samples but the concentration range was much less than the lowest standard addition spike and can only be estimated to ~0.15 ppm in the concrete samples.

7 Determination of Ag, Ba, Ca, Co, Eu, Fe, Li, Mo, Nb, Ni, Sm, Th and U in barite concrete samples

7.1 Procedure

7.1.1 Digestion

The heavy barite concrete for this study was supplied from DD. 120 g of a concrete core, DR2-BOR B-B6-5 was crushed to a fine powder in an agate mortar. The water content of the heavy concrete was determined to 0.5-0.8% after standing overnight at 110 °C and the water content does not significantly contribute to any analytical error. 0.5 g barite concrete sample is dissolved by an acid extraction procedure in a Modblock™ heating unit followed by alkali fusion of the residue. The heavy concrete sample is mixed with 10 ml 40% HF and the solution is evaporated to dryness at 120° C (90° C in the samples) over a 4 hours period. After some cool down the sample is treated with 10 ml 1:1 65% HNO_3/H_2O with heating at 90° C for 1-2 hours. This initial procedure should digest all silicates and dissolve most metal salts from the heavy concrete except $BaSO_4$ and other poorly soluble sulphates. The sample is centrifuged at 4000 rpm for 5 min. and the liquid is transferred and weighted into a polyethylene container. The residue is washed 2 times with 5% HNO_3 and the total volume of the liquid phase in the polyethylene container is ~30 ml (~14% HNO_3).

The solid residue is transferred to a ceramic crucible with 5-10 ml H_2O and the sample is heated to dryness at 110°C. The residue is then fused with 3 g NaOH and 1.5 Na_2CO_3 at 575°C for 3 hours to convert $BaSO_4$ to $BaCO_3$. The fusion cake is allowed to cool down to room temperature. 5-10 ml H_2O is added and the sample is allowed to stand for up to 1 hour. The sample is centrifuged (4000 rpm) for 5 min. and the liquid is collected into a new polyethylene container. The solid residue is treated up to 5 times with 5 ml 0.2 M Na_2CO_3 for 10 min. with heating on a water bath collecting all liquid for further analysis as well. This Na_2CO_3 washing is done to convert all $BaSO_4$ to $BaCO_3$. Finally the solid residue is washed with 2*5 ml H_2O and then dissolved in 0.5 ml 65% HNO_3 and 10 ml H_2O and transferred to a polyethylene container to a total volume of 30 ml (~1% HNO_3). It is preferable to digest three sub-samples to evaluate sample heterogeneity and three blind samples. No reference materials are used for the quality control of this method development because there are none available to our knowledge. Spiked samples can be analysed with the ordinary samples to check the recovery of the analytical method.

7.1.2 Analysis

ICP-OES analysis is used for the determination of ppm to % levels of Ag, Ba, Ca, Eu, Fe, Li and Ni in the samples. To determine all elements in % concentrations the samples are diluted by a factor of 10-100 in 1% HNO_3 prior to analysis, and external calibration from 0.01–20 ppm is used with a multi-element standard containing the elements of interest. Due to the high levels of $BaSO_4$ in the heavy concrete the solution obtained after fusion has to be diluted 2000 times prior to analysis for Ba. For the analysis of Ag, Eu, Li and Ni in ppm concentrations, the solutions are analysed with standard additions calibration with 2–20 (for Eu) and 20–200 ppb spikes. Sc 255.235 and 335.372 nm is used as internal standards (0.1 ppm added to each sample) to correct for matrix effects.

For OES analysis 1.2 kW power and 0.9 L/min nebuliser gas flow is used. For major constituents integration time is 10 s and three replicates are obtained. For the analysis of trace elements 60 s integration time and two replicates are measured.

The elements are analyzed at the following wavelengths (nm) as the sensitivities of the selected lines are sufficient and the amounts of interferences are not causing any problems.

Ag 338.289

Ba 230.424, 233.527, 455.403, 493.408

Ca 315.887, 317.933, 370.602, 396.847, 422.673

Sc 255.235, 335.372

Eu 420.504

Fe 234.350, 238.204, 239.563, 259.940, 261.187, 261.382

Li 670.783

Ni 222.295, 222.486, 231.604

ICP-MS analysis is used for the determination of ppb to ppm levels of Ag, Co, Mo, Nb, Sm, Th and U in the heavy concrete samples. The samples are diluted ~50 times in 1% HNO_3 prior to analysis and calibrated by standard addition of 0.25–5 ppb multi-element standards containing the elements of interest. Rh, In and Bi are used as internal standards in 1-2 ppb concentration. Standard set-up of the ICP-MS instrument is used and the instrument stability is checked prior to analysis.

The elements are analyzed at the following m/z ratios:

Co m/z 59 (4000 resolution)	In m/z 115
Nb m/z 93	Sm m/z 147, 149
Mo m/z 95, 98	Bi m/z 209
Rh m/z 103 (4000 resolution)	Th m/z 232
Ag m/z 107, 109	U m/z 238

7.2 Results

Results for the elements of interest for three different samplings from a concrete core (DR2-BOR B-B6-5) supplied by DD are shown in Table 9. The samplings are on three different dates (050720, 050726 and 050802) and 1-2 samples of 0.5 g were digested. For the samples 050726 and 050802 a spiked sample was analysed with the ordinary samples. The recoveries of spikes added prior to the initial acid digestion (%REC1) or recoveries of spikes from initial digestions with alkali fusion alone (%REC2) are shown in Table 9. The sample 050802 was only extracted with HF/HNO_3 and analysed for trace elements content and spike recoveries. No ICP-MS analysis of the carbonate wash has been done due to the heavy alkaline matrix.

7.3 Conclusion

The analysis of heavy barite concrete shows that the main components in the concrete which may be of interest to DD are Ba (31-34%), Ca (~8%) and Fe (~0.3%). Trace

element concentrations of ~0.1-5 ppm could be determined for Ag, Co, Eu, Li, Mo, Nb, Ni, Sm, Th and U. The uncertainties quoted in Table 9 are for the most part analytical uncertainties and a relative standard deviation of 10% for the trace elements in general is a more realistic estimate since there are no CRMs available to evaluate the accuracy.

Total dissolution is achieved from the developed method for the digestion and analysis of heavy barite concrete, but it is difficult to check the analytical performance because no suitable reference material is available. The recovery of added spikes of the different elements is a way to test the quality of the developed method and for this method the large majority of spike recoveries are in the range 90-110% which is satisfactory. Poorer recoveries are found in some samples (for Eu, Mo and Th), the reason for which is not completely clear since they do not reproduce well. The spikes are almost exclusively recovered after the acid extraction because the spikes are added in solution and are thus easily extracted. Therefore analytical quality of the alkali fusion step is not very well documented. For some elements only alkali fusion have been done, and for Eu and Ni recoveries of 97% and 79% have been determined.

Table 9 Results for the analysis of heavy barite concrete.

Barite concrete

ELEMENT	SAMPLE	N	Spike	Acid extraction	%REC1	Alkali fusion	%REC2	Carbonate wash	Sum
Barium	050720	2	0	*5941±1547*		*33.4±4.0%*		*1526±38*	**34.2±3.8%**
	050726	3	0	*7689±1030*		*32.7±4.2%*		*1067±235*	**31.4±2.1%**
	050802	2	0	-		-			
Calcium	050720	2	0	*5.40±0.03%*		*2.23±0.14%*		*701±47*	**7.70±0.18%**
	050726	3	0	*5.31±0.35%*		*2.49±0.39%*		*438±115*	**7.85±0.38%**
	050802	2	0	-		-			
Cobalt	050720	2	0	*1.01±0.03*		*<LOD*		-	**1.01±0.03**
	050726	3	1	*1.4±0.5*	*101%*	*<LOD*		-	**1.4±0.5**
	050802	2	1	*1.04*	*94%*	-		-	**1.04**
Europium	050720	2	0	*0.215±0.001*		*0.49±0.11*		-	**0.70±0.11**
	050726	3	1	*0.261±0.009*	*101%*	*0.56±0.08*	*97%*	-	**0.80±0.09**
	050802	2	1	*0.219*	*121%*	-		-	**-**
Iron	050720	2	0	*2866±14*		*22±20*		*59±7*	**2947±14**
	050726	3	0	*2858±27*		*14±5*		*29±4*	**2901±31**
	050802	2	0	-		-		-	
Lithium	050720	2	0	*3.52±0.06*		*<LOD*		*<LOD*	**3.52±0.06**
	050726	3	1	*3.40±0.15*	*101%*	*<LOD*		*<LOD*	**3.40±0.15**
	050802	2	1	*3.69*	*105%*	-		*<LOD*	**3.69**
Molybdenum	050720	2	0	*0.26±0.04*		*<LOD*		-	**0.26±0.04**
	050726	3	1	*1.11±0.03*	*120%*	*<LOD*		-	**1.11±0.03**
	050802	2	1	*0.53±0.02*	*94%*	-		-	**0.53±0.02**
Nickel	050720	2	0	*2.38±0.04*		*3.1±0.6**		*<LOD*	**2.38±0.04**
	050726	3	1	*2.6±0.5*		*2.7±0.1**	*79%*	*<LOD*	**2.6±0.5**
	050802	2	1	*2.53±0.06*	*106%*	-		*<LOD*	**2.53±0.06**
Niobium	050720	2	0	*0.62±0.004*		*<LOD*		-	**0.62±0.004**
	050726	3	1	*0.67±0.04*	*101%*	*<LOD*		-	**0.67±0.04**
	050802	2	1	*0.73*	*95%*	*<LOD*		-	**0.73**
Silver	050720	2	0	*4.42±0.02*		*<LOD*		*<LOD*	**4.42±0.02**
	050726	3	1	*5.57±0.06*	*92%*	*<LOD*		*<LOD*	**5.57±0.06**
	050802	2	1	*4.18*	*100%*	*<LOD*		*<LOD*	**4.18**
Samarium	050720	2	0	*0.44±0.03*		*1.7±0.1*		-	**2.1±0.1**
	050726	3	1	*0.47±0.004*	*95%*	*1.7±0.1*		-	**2.2±0.1**
	050802	2	1	*0.38±0.02*	*108%*	-		-	**-**
Thorium	050720	2	0	*0.329±0.001*		*0.030±0.001*		-	**0.359±0.002**
	050726	3	1	*0.35±0.01*	*82%*	*0.08±0.07*		-	**0.43±0.07**
	050802	2	1	*0.36*	*94%*	-		-	**0.36**
Uranium	050720	2	0	*0.26±0.01*		*0.04±0.05*		-	**0.30±0.05**
	050726	3	1	*0.27±0.01*	*99%*	*0.030±0.001*		-	**0.30±0.01**
	050802	2	1	*0.26*	*94%*	-		-	**0.26**

All concentrations are in ppm unless noted otherwise
Uncertainty = 1 standard deviation
N = Number of samples digested
Spike = Number of spiked samples
%REC1 = Spike recovery for the acid extraction followed by fusion
%REC2 = Spike recovery for sample digestion by fusion alone
Sum = The total concentration of the element in the sample
***Impurity from the fusion reagents**

As a further check of the developed method several sample digestions have been done and the results from different digestions are in excellent agreement for the large majority of elements. Reported concentrations for Mo and to some extent Ag show a significant variation, which may be due to sample inhomogeniety for those elements (nugget effect). The analysis for Mo is done by ICP-MS and during the analysis a large background contamination from Mo was observed which accounts for up to 50% of the observed signal. This, and the fact that one of the four method blank samples were contaminated with what corresponds to 0.7 ppm Mo more than the average of the remaining method blanks may also serve to explain some of the variance in the reported results. The analytical result for Mo should be taken as a guideline only and may differ as much as factor 2. If better accuracy for the analysis of Mo is needed then a separate analysis for Mo is necessary.

The uncertainty in the analysis of Ba is large considering that the concentration of Ba is above 30%. This uncertainty is primarily related to the fusion step and must be due to unknown losses in the process of repeated washes, centrifugations etc.

8 Conclusion

Methods for the accurate determination of stable isotopes of elements in construction materials with relevance to the work of the Danish Decommissioning have been developed.

Prior to the analysis the elements of interest must be released from the construction materials and this is done with several different digestion methods. For the analysis of aluminium, lead, graphite and steels the samples are digested with mineral acids and microwave heating at increased pressures in a sealed teflon vessel. The aluminium, lead and steel are fully dissolved after the digestion procedure whereas graphite is chemically inert to the acid treatment used, but the elements of interest are extracted from the graphite quite efficiently. Concrete is digested with open-vessel heating in a Modblock™ digesting unit in a two step procedure involving 40% HF followed by 32% HNO_3. The heavy barite concrete is first treated as the concrete samples but a large residue of poorly soluble sulphates (mainly $BaSO_4$) is left. The residue is fused with $NaOH/Na_2CO_3$ at 575°C and after some work up the product from the fusion is dissolved in dilute HNO_3.

After the release of the elements from the materials, the samples are analysed by ICP-OES and ICP-MS multi-element analysis. In general the following elements are of interest to DD; Ag, Ba, Ca, Co, Eu, Fe, Li, Mo, Nb, Ni, Sm, Th and U. For graphite, steel, concrete and heavy concrete, analytical methods for the determination of all 13 elements have been developed (except Ca in steel). For aluminium and lead methods for the determination of Ag, Co, Li, Nb, Ni and U, as well as Ba in the lead have been developed.

When possible the methods have been verified against certified reference materials and calibration with standards additions and internal standard corrections have been used to correct for matrix effects most efficiently. The accuracy has also been checked with spikes when reference materials are not available. For the aluminium, lead, graphite and stainless steel, reference materials are available and used in the development. A Portland cement reference material is used in the development of the

analytical methods for concrete material, whereas no reference material is available for the method development for the heavy concrete material. Whenever reference materials are used good agreement between measured and certified concentrations is observed.

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